Investigation of C_{60}/NMP and C_{60}/NMP/xylene solutions by absorption spectroscopy and dynamic light scattering

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Методами УФ-видимой спектроскопии и динамического рассеяния света (ДРС) изучено поведение межмолекулярных взаимодействий в свежих и состаренных растворах фуллерена C_{60} в чистом N-метил-2-пирролидоне (NMП), а также в смешанных растворителях NMП/ксилол. Экспериментально показано, что старение раствора C_{60}/NMП приводит к исчезновению характерного максимума молекулярного поглощения при ~330 нм со сглаживанием и к увеличению интенсивности оптического поглощения. Последние зависят от образования комплексов C_{60}-NMП, а также от перехода молекул фуллеренов в нанокластерное состояние. Увеличение содержания ксилола в C_{60}/NMП/ксилол приводит к значительным изменениям переноса заряда между растворенным веществом и растворителем (C_{60}-NMП, C_{60}-C_{60}) при фиксированной концентрации фуллерена. Последнее приводит к реорганизации наночастиц, которая протекает с разрушением молекулярных комплексов. При этом методом ДРС установлено, что геометрические размеры синтезированных нанокластеров C_{60} уменьшаются.

Ключевые слова: фуллерен C_{60}, бинарный раствор, сольватация, агрегация, нанокластер, электронные спектры поглощения, гидродинамический диаметр.

The behavior of intermolecular interactions in fresh and aged solutions of fullerene C_{60} in neat N-methyl-2-pyrrolidone (NMP), as well as in NMP/xylene mixed solvents, were studied by the methods of ultraviolet-visible spectroscopy and dynamic light scattering (DLS). It has been experimentally shown that the aging of the C_{60}/NMP solution leads to the disappearance of the characteristic maximum of molecular absorption at ~330 nm with smoothing, as well as to an increase in the optical absorption intensity. The latter depend on the formation of "C_{60}-NMP"complexes, as well as on the transition of fullerene molecules to the nanocluster state. Increasing the xylene content in the C_{60}/NMP leads to significant changes in charge transfer between solute and solvent ("C_{60}-NMP", "C_{60}-C_{60}") at a fixed concentration of fullerene. The latter leads to the reorganization of nanoparticles, which proceeds with the destruction of molecular complexes. In this case, using the DLS method, it was found that the geometric dimensions of the synthesized C_{60} nanoclusters decrease.

Keywords: fullerene C_{60}, binary solution, solvation, aggregation, nanocluster, electronic absorption spectra, hydrodynamic diameter.

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I. Introduction

In recent years, interactions of fullerene molecules (C_{60}, C_{70}) with various single and multicompo-

nent solvents have been actively studied [1-2]. One of the features of fullerenes is their ability to form compounds (complexes) of the donor-acceptor type when dissolved in various organic and inorganic solvents [3-4]. On the other hand, scientific studies carried out by various groups show the unusual behavior of fullerenes in such solutions, associated with the formation of clusters of fullerene molecules [5-7]. Due to the widespread use in scientific laboratories of the world of unique transmission electron microscopes with a fully automated robot for vitrification for ultrafast freezing (more than 10^3 C/sec) of solutions, experimental methods of X-ray diffraction analysis, mass spectrometry and dynamic light scattering, interest in research has revived the previously unexplored physical-chemical properties of fullerenes in various solvents [8-12]. The results of these studies turned out to be useful for the synthesis of more complex nanosized crystalline and porous (fractal) materials of a new generation with new physical-chemical properties [13-15]. At the same time, the specific limiting conditions for the complexation of fullerene and solvent molecules, as well as for the clustering of fullerene molecules upon dissolution in solutions, remain poorly understood.

The aim of this work is to study the patterns of intermolecular interaction in solutions of C_{60} fullerene in N-methyl-2-pyrrolidone (NMP) with the addition of a low-polarity solvent (xylene) by optical spectroscopy and dynamic light scattering (DLS).

II. Materials and methods

C_{60} fullerene (>99.8% purity) was added to N-methyl-2-pyrrolidone (C_5H_9NO) and mixed intensively using a programmable laboratory magnetic stirrer «MS-11 H» (WIGO, Poland) for thirty minutes until solution become mauve. Solutions of C_{60}/NMP/xylene with different volume fractions of xylene (C_8H_{10}) were obtained by adding xylene to a solution of C_{60}/NMP. All used reagents are received from the supplier Sigma Aldrich (USA). The maximum solubility of the crystalline C_{60} fullerene powder in xylene ~7.7 mg/ml and N-methyl-2-pyrrolidone (NMP) is ~0.89 mg/ml. The initial C_{60} concentration for the C_{60}/NMP solutions was taken as ~0.2 mg/ml to avoid the dissolution saturation effects that can occur when mixing solutions with different maximum solubility. During the experiments fullerene C_{60} solutions were stored in a dark chemical cabinet. All the experiments described below were carried out at room temperature (T≈24±1°C).

The electronic absorption spectra of studied solutions were obtained with the Shimadzu UV-2700 spectrometer (Shimadzu, Japan) in a wavelength range of 200–1000 nm. Quartz «K-10» cells with 1 cm path length were used.

The hydrodynamic sizes of nanoclusters mC_{60} (where m is the number of C_{60} molecules in a synthesized nanocluster) were measured via dynamic light scattering using a Zetasizer Nano ZEN3600 (Malvern Instruments Ltd.) with a scattering angle of 173°. The DLS instrument is equipped with a 5 mW He-Ne laser operating at a wavelength of 633 nm.

III. Experimental results and their discussion

We investigated the physical features of the behavior of the optical absorption spectra of a C_{60} solution in a nitrogen-containing solvent (NMP) with the addition of a weakly polar solvent (xylene) to the initial C_{60} solution. Figure 1 shows the evolution of the optical absorption spectra of a freshly prepared C_{60}/NMP solution with the addition of xylene in various proportions. The spectra are referred to one fullerene concentration in solution (~0.2 mg/ml). At relatively high concentrations of C_{60}/NMP solutions, a solvate shell consisting of NMP molecules forms around fullerene molecules. The formation of a solvation shell around C_{60} molecules with charge transfer by an NMP molecule is confirmed by surface Raman scattering [16].

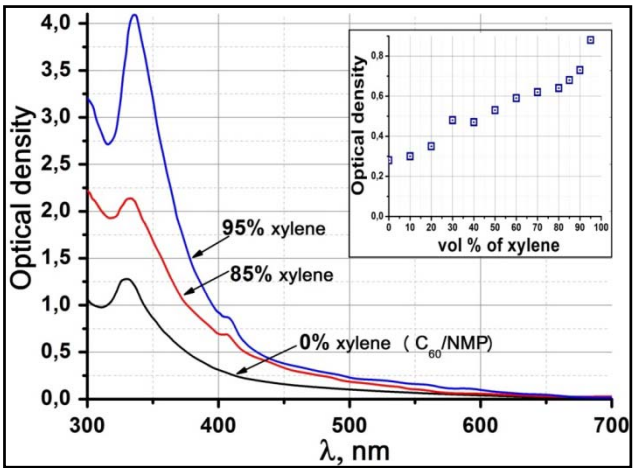


Figure 1. UV–V is spectra of a freshly prepared C_{60}/NMP solution when xylene is added in various volume proportions. The inset shows dependence of optical density at a wavelength of ~407 nm versus xylene volume fraction in the mixture. The initial concentration of C_{60} in the solution of C_{60}/NMP was ~0.2 mg/ml.

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It can be seen that the optical absorption spectra of C_{60}/NMP change sharply with a change in the volume percent of xylene, namely, there is an increase in the amplitude of the spectrum and a shift of the characteristic peak λ≈330 nm to the long-wavelength region of the spectrum (positive solvatochromic effect, up to ~6.14 nm). It should be noted that in this case a batochromic shift of the characteristic absorption maximum occurs due to the proportional mixing of the two solvent components (NMP and xylene) with the C_{60} fullerene molecules. In the high volume proportions of xylene (≥85 vol.% of xylene), the characteristic absorption maximum at ~407 nm is also restored in the spread spectrum of the C_{60}/NMP solution. This is due to the good solubility of C_{60} in xylene, which means the loss of the solvate shell formed at NMP. At this point, the absorption amplitude at ~407 nm suddenly increases up to 80 vol.% of xylene and the coupling deviates from the linearity from 85 vol.% of xylene in solution (see inset to Fig. 1).

It can be noted that the initial optical absorption spectrum of the C_{60}/NMP solution smoothes over time, which confirms the optical spectrum obtained during 36-hour storage of the solution (see Fig. 2, C_{60}/NMP spectrum).

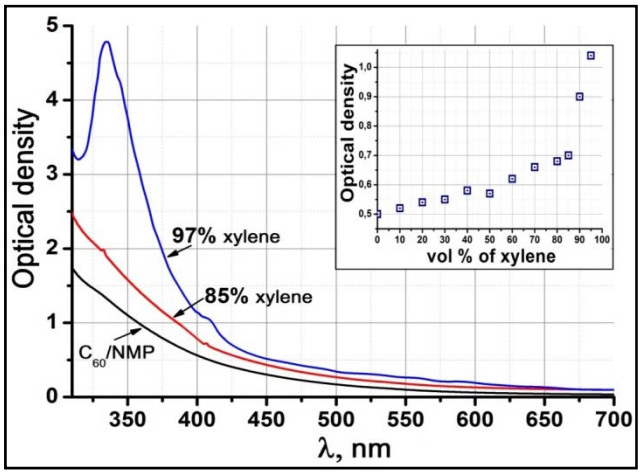


Figure 2. Evolution of the electron absorption spectra of C_{60}/NMP solution after its 36-hours storage with the addition of xylene in various volume ratios. The inset shows the dependence of the optical density at a wavelength of ~407 nm versus the contents of xylene in the C_{60}/NMP. The initial concentration of C_{60} in the solution was ~0.2 mg/ml.

The disappearance of the characteristic maximum at ~330 nm and an increase in the absorption intensity during storage of the solution for 36 hours may be associated with an increase in the processes of solvation and self-organization of C_{60} molecules during the aging of solutions, which ultimately lead to the formation of nanosized clusters of fullerene C_{60}. Next, we investigated the effect of adding xylene (up to 97 vol.%) to this aged solution (C_{60}/NMP) in order to establish a critical concentration of xylene in the solution to restore the characteristic absorption maximum at ~330 nm. It was found in experiments that with increase in the xylene content up to vol. 80% in the aged solution of C_{60}/NMP, a slow change in the amplitude of the optical spectrum is observed. In about 85 vol.% xylene in solution weak characteristic absorption maxima begin to appear at ~332 nm and ~406 nm. This means that the solvate shell "C_{60}+NMP" begins to disappear from this critical fraction of xylene in C_{60}/NMP. A sharp increase in the amplitude of the spectrum begins with ~90 vol.% xylene (see inset to Fig. 2), and the restoration of characteristic peaks with a shift towards the corresponding position of the maximum of the C_{60}/xylene solution at ~97 vol.% added xylene in aged solution of C_{60}/NMP (see Fig. 2). In this case, the addition of xylene as a low-polarity component in the C_{60}/NMP system promotes both the selective solvation of C_{60} fullerene by solvent molecules (NMP) and the reorganization of C_{60} nanoclusters. The solvate shell begins to break down only when the xylene content is close to a pure C_{60}/xylene solution.

Figure 3 shows experimental DLS results for an aged C_{60}/NMP solution (after 36 hours of storage) compared after adding xylene at 85 vol.% in solution.

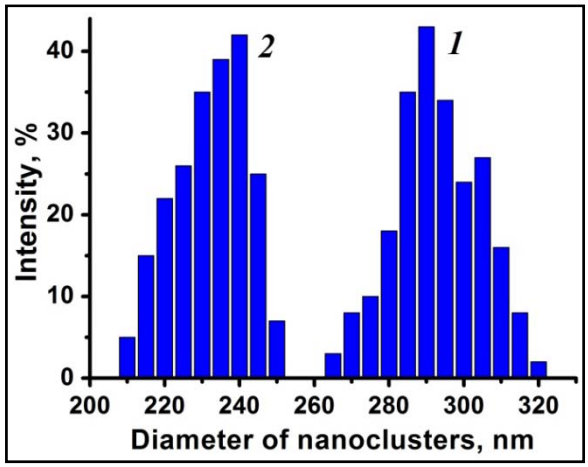


Figure 3. Distribution by hydrodynamic diameters of C_{60} nanoclusters in C_{60}/NMP solution after its 36-hours storage (histogram 1) and after adding xylene at 85 vol.% to aged C_{60}/NMP (histogram 2). The initial concentration of C_{60} in solutions was ~0.2 mg/ml.

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The main fraction of light-scattering fullerene nanoparticles in C_{60}/NMP solution is distributed in the diameter range ~265÷320 nm, and the maximum distribution of C_{60} fullerene clusters is localized in the region of ~290 nm (Fig. 3, histogram 1).

It can be noted that C_{60} nanoclusters synthesized in a 36 hours C_{60}/NMP solution contain a large number of NMP molecules in the form of complexes of C_{60} and NMP molecules. The maximum value of the hydrodynamic diameter of a light scattering fullerene particle after adding xylene at 85 vol.% in C_{60}/NMP solution decreases and shifts by ~240 nm, and the range of hydrodynamic sizes of C_{60} nanoclusters corresponds to ~210÷250 nm (Fig. 3, histogram 2). The addition of a weakly polar solvent (xylene) to a C_{60}/NMP solution leads to the reorganization of nanoparticles, which occurs with partial destruction of complexes of C_{60} and NMP molecules. It can be seen that after the reorganization of C_{60} nanoparticles in this solution, the geometric dimensions of C_{60} nanoclusters decrease than in a C_{60}/NMP solution.

The use in experiments of fresh and aged C_{60}/NMP solutions, as well as after adding xylene to them with varying the volume fraction in the range of ~5–97 vol.% made it possible to obtain valuable information about the intermolecular interactions "solute-solvent" and "solute-solute" in solutions. The obtained scientific results are important for the effective use of fullerene solutions, especially in the fields of nanotechnology, requiring controlled and selective liquid disperses systems.

IV. Conclusion

The shape and characteristics of the optical absorption spectra of freshly prepared and aged solutions of C_{60} in NMP were determined. It has been established that the disappearance of the maximum at $\lambda \approx 330$ nm with smoothing and an increase in the intensity of optical absorption with the aging of the C_{60}/NMP solution may depend on the formation of new complexes C_{60}-NMP, as well as on the transition of fullerene from the molecular to the state of the nanocluster.

The physical features of the behavior of the optical absorption spectra of freshly prepared and aged C_{60} solutions in NMP with the addition of xylene were studied by optical spectroscopy. It has been established that the observed changes (batochromic shift of characteristic maxima, increase in intensity, and smoothing) of the absorption spectra of C_{60}/NMP solutions by changing the solvent composition strongly depend on the age of the solutions.

The addition of xylene to the aged C_{60}/NMP solution leads to the reorganization of nanoparticles, which proceed with the partial destruction of the C_{60}-NMP complexes. Using the DLS method, it was found that after the reorganization of nanoparticles in solution, decreasing in the geometric dimensions of the synthesized C_{60} nanoclusters occur.

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C_{60}/НМП ва C_{60}/НМП/ксилол эритмаларини ютилиш спектроскопияси ва ёруғликнинг динамик сочилиши усулларида тадқиқ қилиш

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C_{60} фуллереннинг соф Н-метил-2-пиролидон (НМП) даги янги ва эски эритмаларида, шунингдек, НМП/ксилол аралашмасидаги эритмаларидаги молекулалараро ўзаро таъсирларнинг ҳолати УБ-кўринадиган спектроскопия ва ёруғликнинг динамик сочилиши (ЁДС) усулларида ўрганилди. C_{60}/НМП эритмасининг эскириши оптик ютилиш спектрида ~330 нм га мос келувчи характерли молекуляр ютилиш максимумининг силлиқланиб йўқолишига, шунингдек, оптик ютилиш интенсивлигининг ошишига олиб келиши экспериментал равишда кўрсатилди. Бу ўзгаришлар «C_{60}-НМП» комплексларининг шаклланишига, шунингдек фуллерен молекулаларининг нанокластер ҳолатига ўтиши билан боғлиқ. C_{60}/НМП/ксилол таркибидаги ксилол миқдорини ошириш фуллерен концентрацияси доимий бўлганда эриган модда ва эритувчи («C_{60}-НМП», «C_{60}–C_{60}») ўртасида заряд алмашинишида сезиларли ўзгаришларга олиб келади. Бу ҳолат эритмадаги молекуляр комплексларнинг йўқолиши билан давом этадиган нанозаррачаларнинг қайта ташкил бўлишига олиб келади. Бу ҳолда ЁДС усулида эритмада синтезланган C_{60} нанокластерлар геометрик ўлчамлари камайиши аниқланди.

Калит сўзлар: C_{60} фуллерен, бинар эритма, солватация, агрегация, нанокластер, электрон ютилиш спектрлари, гидродинамик диаметр.

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